REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

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1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE** Technical Papers	**3. DATES COVERED** *(From - To)*
4. TITLE AND SUBTITLE		**5a. CONTRACT NUMBER**
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		**5d. PROJECT NUMBER** 2303
		5e. TASK NUMBER M2C8
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048		**8. PERFORMING ORGANIZATION REPORT**
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048		**10. SPONSOR/MONITOR'S ACRONYM(S)**
		11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

1121 026

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Leilani Richardson
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	A		**19b. TELEPHONE NUMBER** *(include area code)* (661) 275-5015

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TP-FY99-Ø116

✓ Spreadsheet
✓ DTS

MEMORANDUM FOR PRR (~~Contractor~~/In-House Publication)

FROM: PROI (TI) (STINFO) 1 June 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-FY99-0116**
Tam and Fajardo., "Measurement of Large Dopant Concentrations by Dopant-Induced Infrared Activity in Solid Parahydrogen"

Poster Session HEDM CONFERENCE **(Public Release)**

HIGH ENERGY DENSITY MATTER CONTRACTORS CONFERENCE
Cocoa Beach, FL 8-11 June 1999

Measurement of Large Dopant Concentrations by Dopant-Induced Infrared Activity in Solid Parahydrogen

Simon Tam and Mario E. Fajardo
U.S. Air Force Research Laboratory, Propulsion Directorate
(AFRL/PRSP, 10 E. Saturn Blvd., Edwards AFB CA 93524-7680)
simon_tam@ple.af.mil
mario_fajardo@ple.af.mil

High Energy Density Matter (HEDM) Cryosolid Propellants

HEDM Cryosolid Program Objectives

Trap 5% molar concentration of energetic additives in solid hydrogen.
Demonstrate size-scaleable sample production method.

Payoffs

Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

LOX/LH_2: $I_{sp} = 390$ s
5% B/H_2 + LOX: $I_{sp} = 500$ s (+30%)*

*calculated for $P_{chamber} = 1000$ ~~PSIA~~ *oc*, $P_{exhaust} = 14.7$ ~~PSIA~~ *oc*

Greater Propellant Density

$$\begin{aligned} \text{liquid } H_2 &: \; = 0.070 \text{ g/cm}^3 \\ \text{solid } H_2 &: \; = 0.087 \text{ g/cm}^3 \; (+25\%) \\ \text{50/50 liquid He/solid } H_2 &: \; = 0.105 \text{ g/cm}^3 \; (+50\%) \end{aligned}$$

TASK OBJECTIVE

Develop a technique for quantifying dopant species identities and concentrations in optically dense samples using the dopant-induced infrared (IR) absorptions.

BACKGROUND

Have demonstrated we can produce gram scale samples of solid pH_2 doped with HEDM species with concentrations of 0.01 to 0.1%.

Dopants were produced using laser ablation which is not a suitable method for producing high concentrations.

Three teams in the Cryosolids Working Group tasked with: 1) developing new dopant sources; 2) developing a diagnostic for characterizing the new sources; and **3) developing diagnostic tools for detecting the~~n~~ products of these new sources in pH_2.**

APPROACH

Direct absorption measurements of thick, heavily concentrated samples of HEDM doped pH_2 solids will not work as a diagnostic for these new sources.

Alternative is to use the dopant-induced IR absorptions as a diagnostic.

Beer's Law

$$A(\tilde{\nu}) \equiv 2.303 \quad \log_{10}\left(\frac{I_0}{I}\right) = \alpha c l$$

$$c = \frac{A(\tilde{\nu})}{\alpha\, l} \Rightarrow \frac{2.303 \int_{band} \log_{10}\left(\frac{I_0}{I}\right) d\tilde{\nu}}{l \int_{band} \alpha(\tilde{\nu})\, d\tilde{\nu}}$$

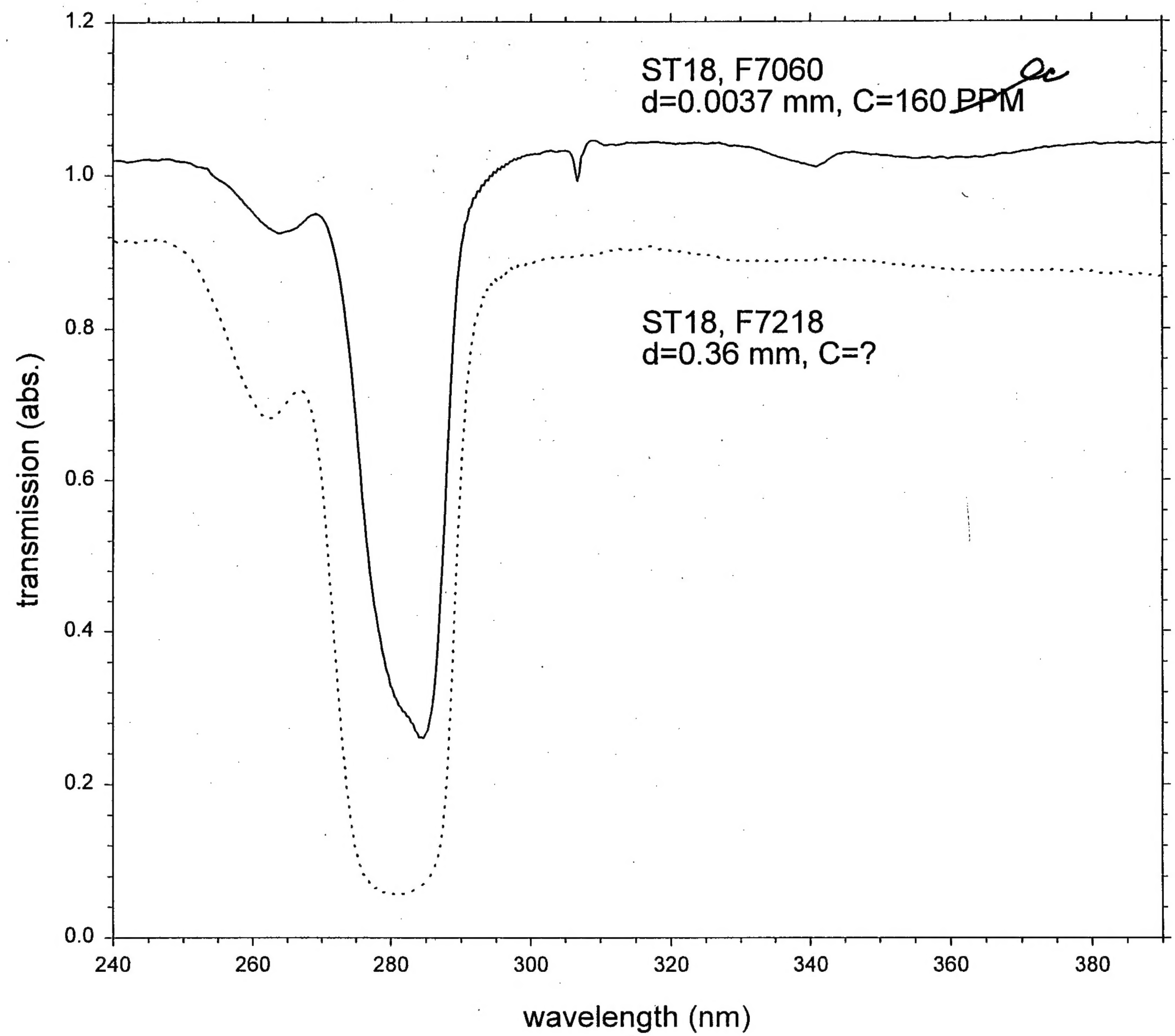
Increased path lengths or highly concentrated samples can cause saturation of the absorption.

If we want to work with gram scale, heavily-doped pH_2 samples, we require a spectral feature that has a very small intrinsic absorption coefficient (α) to compensate for the higher c and l.

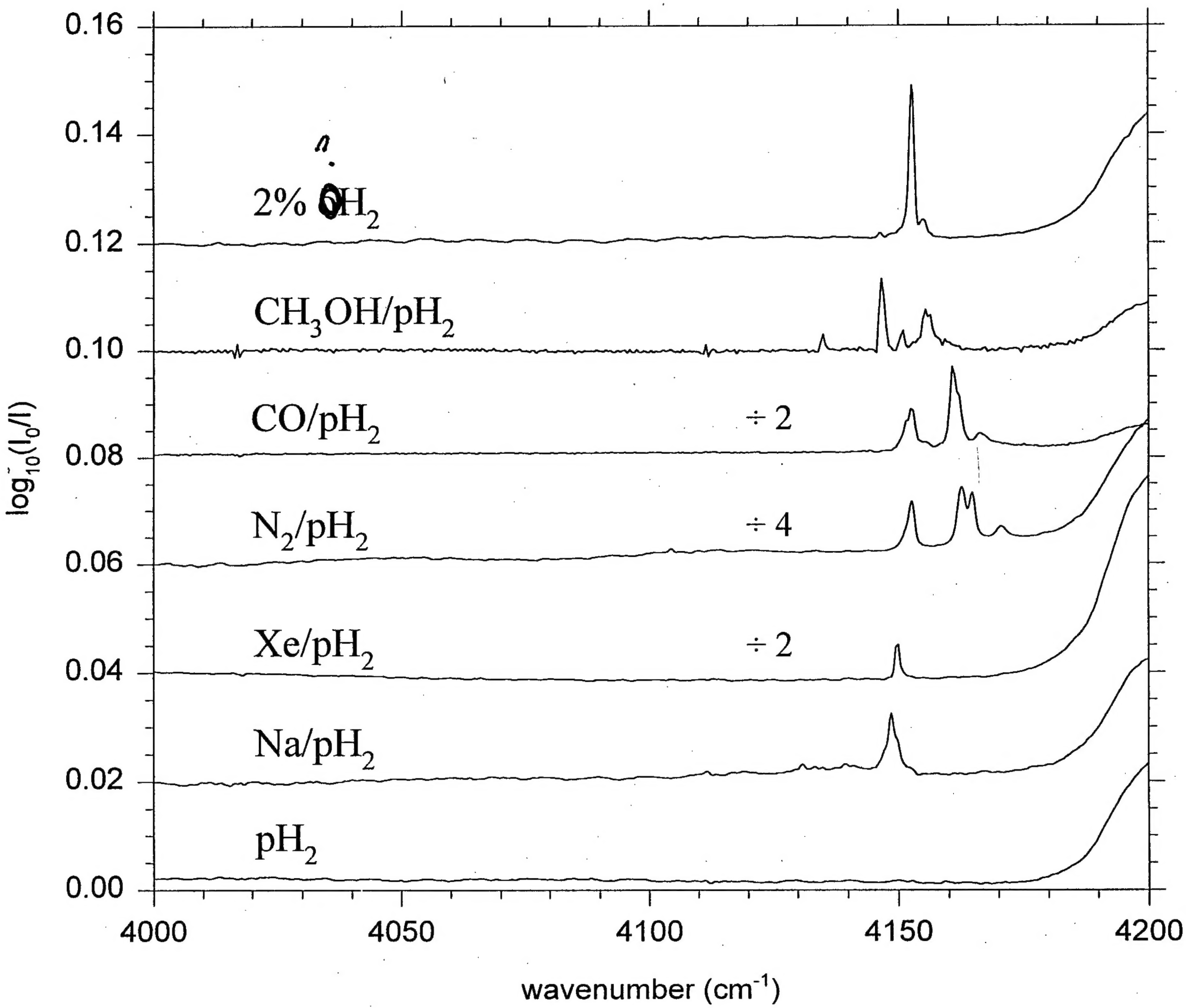
We can use dopant-induced infrared absorptions to determine the concentration.

BUT: Need to determine $\alpha_{ind} \equiv$ the dopant-host intrinsic absorption strength

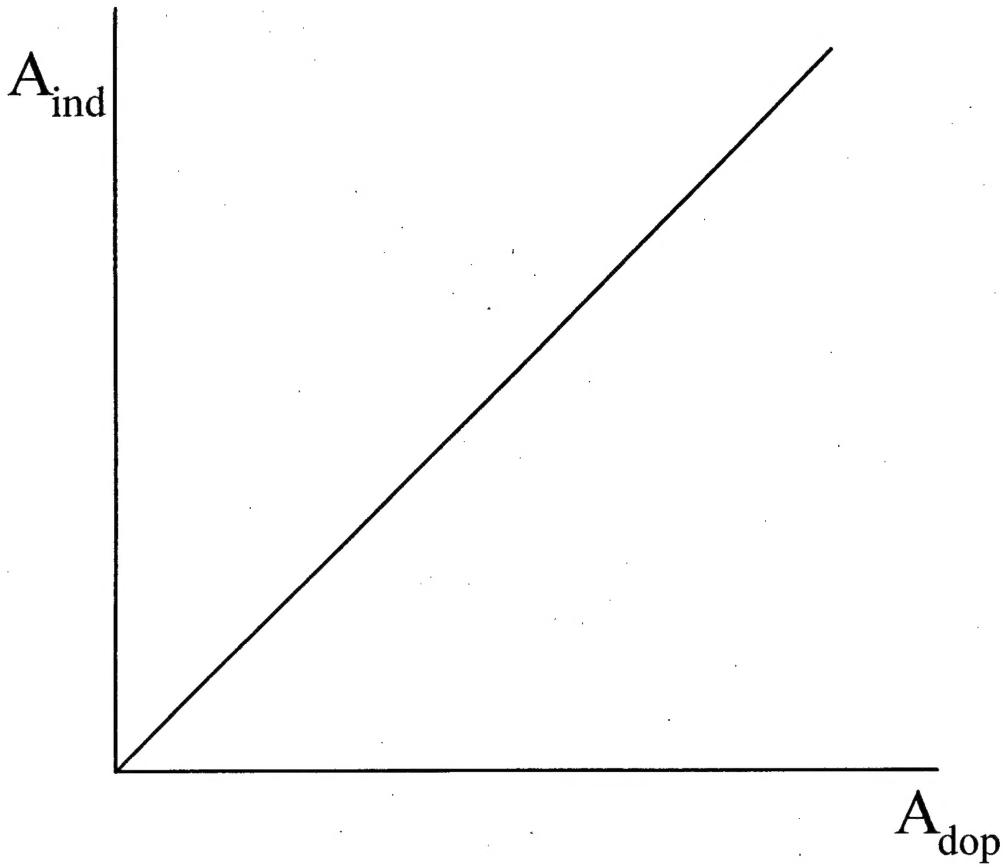
Mg/pH_2 and Mg/oD_2, T=2K



Examples of Dopant Induced H_2 Absorptions



Determining α_{ind} from α



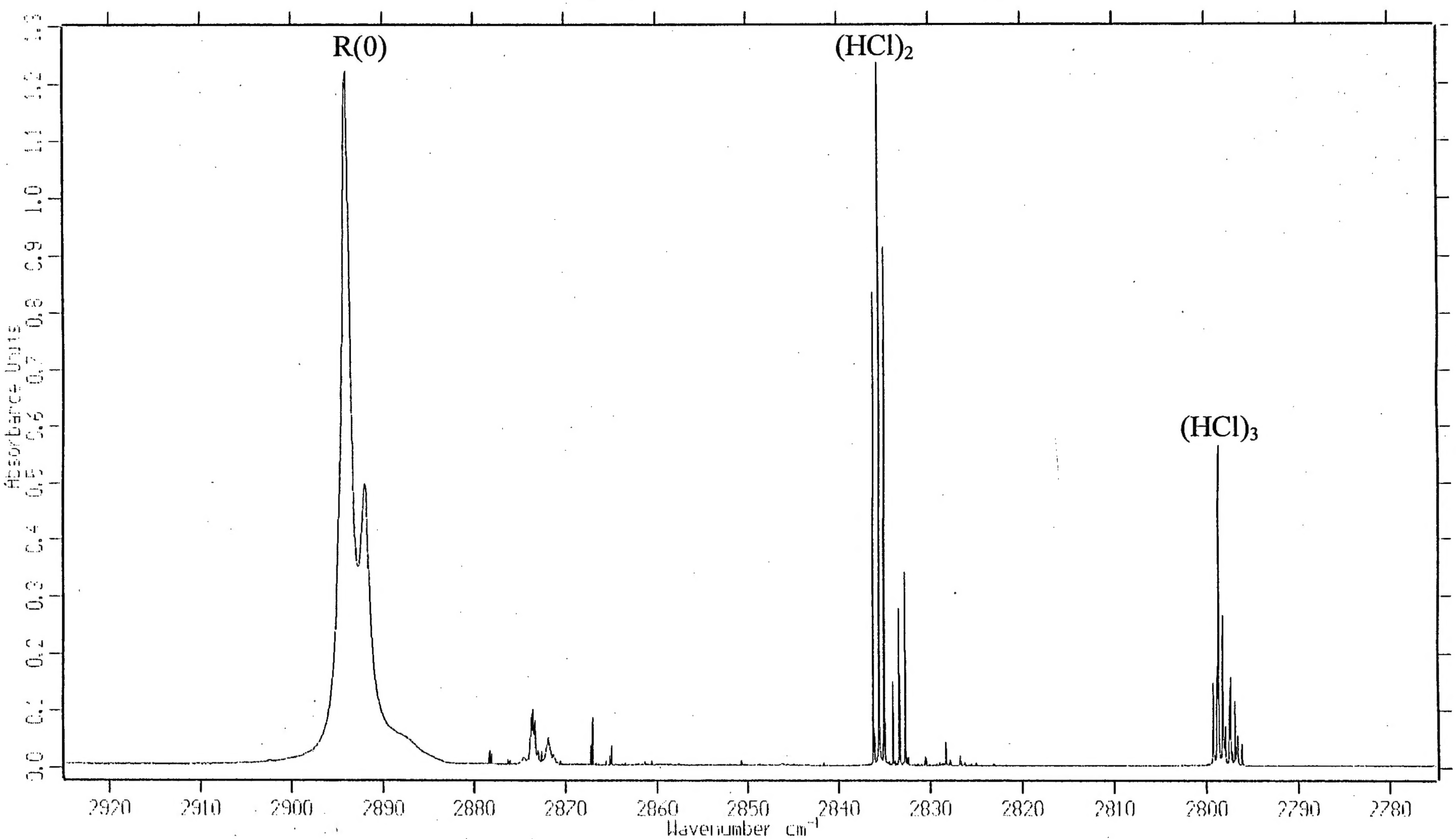
Where:

$$\text{Slope of the line} = \frac{\alpha_{ind}}{\alpha}$$

$\alpha \equiv$ property of the dopant in the gas phase

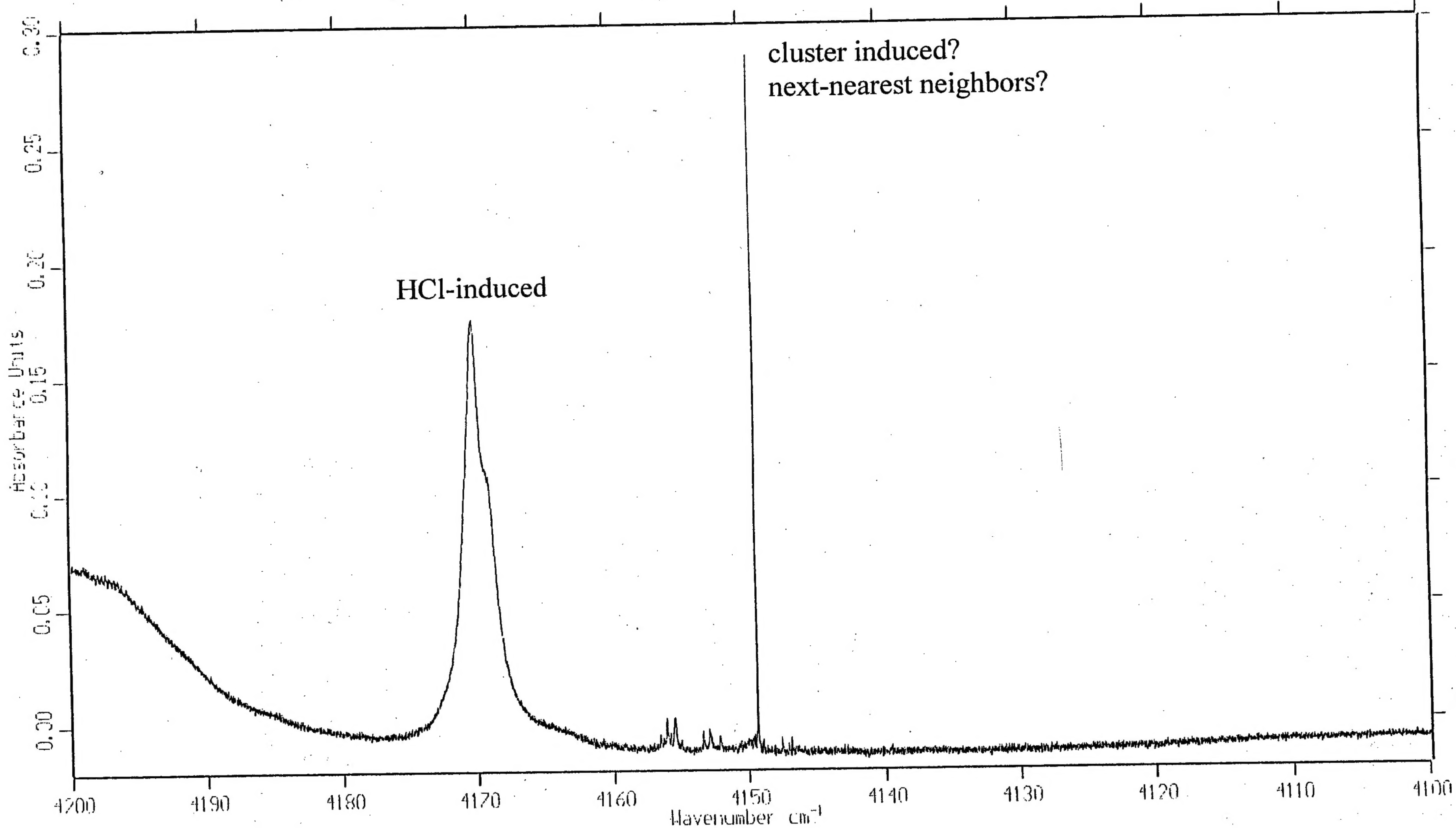
$\alpha_{ind} \equiv$ property of the dopant and pH_2 in solid pH_2

HCl/pH_2 at 2.4 K, 88 ppm, Resolution = 0.0075 cm^{-1}
Annealed Sample, HCl Absorptions Region



ST27061.11

HCl/pH_2 at 2.4 K, 494 ppm, Resolution = 0.0075 cm^{-1}
As Deposited Sample, Induced Absorption Region



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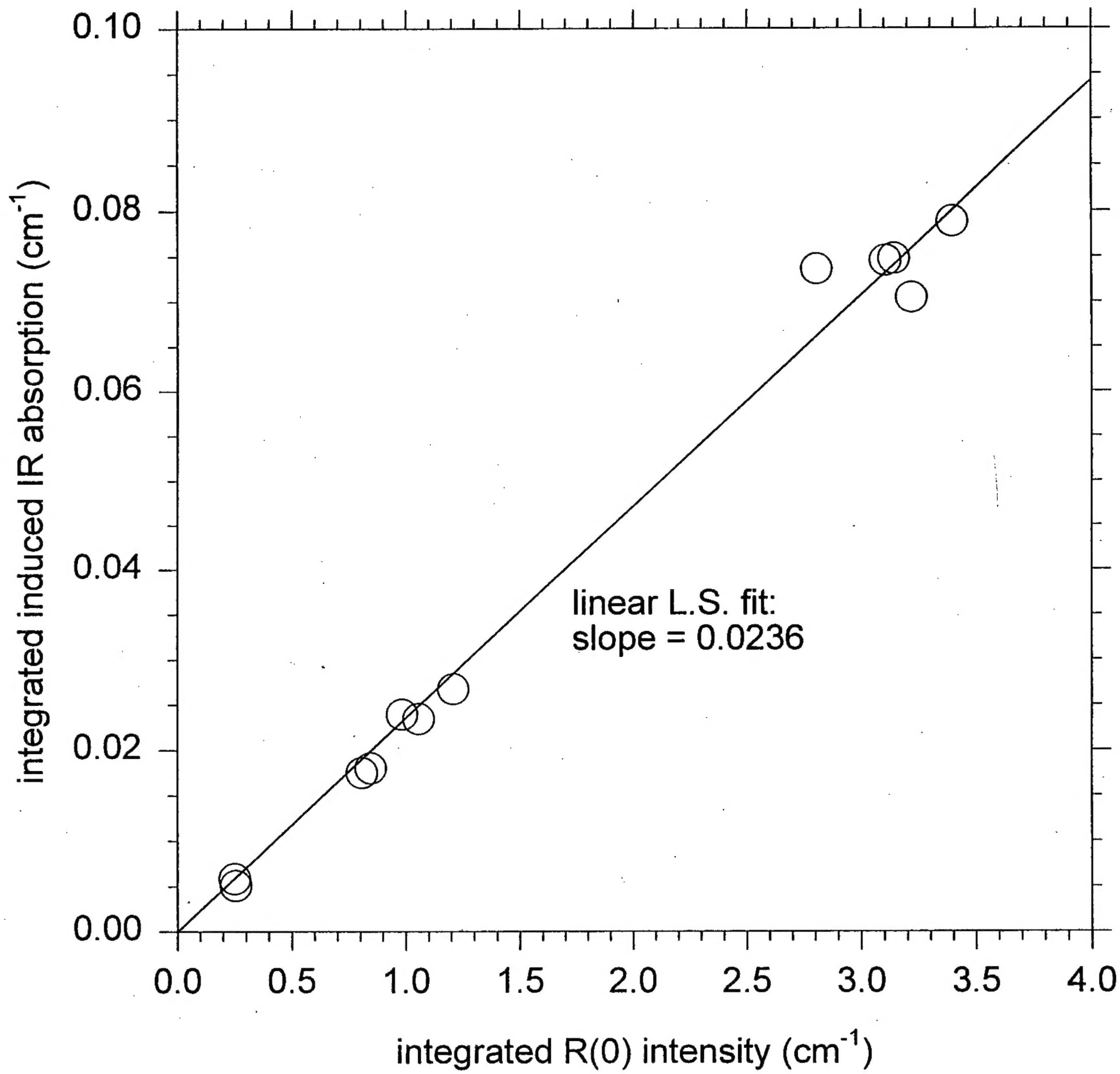
Correlation between HCl-Induced pH_2 IR Absorption and HCl R(0) Absorption



HCl-Induced pH_2 Intrinsic IR Absorption Strength

$$\int \alpha_{ind}(HCl/pH_2)d\nu = 0.0236 \int \alpha(HCl)\, d\nu$$

literature: $\int \alpha(HCl)\, d\nu = 32$ km/mol

$\therefore \quad \int \alpha_{ind}(HCl/pH_2)\, d\nu =$ **<u>0.75 km/mol</u>**

Question: What is the maximum, measurable concentration of HCl/pH_2?

Assume: a) 1 mm thick sample

b) $\int A_{max}\, d\nu = 2\ cm^{-1}$

Answer:

$$c_{max} = \frac{2.303\ (2\ cm^{-1})}{(0.1\ cm)(7.5x10^{-4}\ \frac{cm}{mol})}$$

$= 6.2 \times 10^{-4}$ mol/cm^3

$\Rightarrow 1.4\%\ HCl/pH_2$

SUMMARY

For millimeters thick, heavily-doped samples, direct absorption spectroscopy fails because of limitations on dynamic range and achievable signal-to-noise levels.

Dopant-induced pH_2 transitions are a possible solution to this problem.

1) appear to obey Beer's Law
2) are very weak IR transitions (i.e., increased dynamic range for heavily doped samples)

For HCl in pH_2, the intrinsic absorption strength is approximately 2.4% of the intrinsic absorption strength of HCl in the gas phase.

Can calculate the maximum measurable concentration for a HCl-doped pH_2 solid: 1.4% for a 1-mm thick sample, achieving objective of measuring ~1% concentration in millimeters thick samples.

FUTURE DIRECTIONS

We are in the process of completing a survey of various dopants in solid pH_2 to determine the generality of using the induced absorptions for concentration measurements.